

A unifying model for chemical and colloidal gels

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We investigate the slow dynamics in gelling systems by means of MonteCarlo simulations on the cubic lattice of a minimal statistical mechanics model. By opportunely varying some model parameter we are able to describe a crossover from the chemical gelation behaviour to dynamics more typical of colloidal systems. The results suggest a novel connection linking classical gelation, as originally described by Flory, to more recent results on colloidal systems. PACS: 05.20.-y, 82.70.Gg, 83.10.Nn

The chemical gelation transition, as it is typically observed in polymer systems, transforms a solution of polymeric molecules, the sol, from a viscous fluid to an elastic disordered solid, the gel. The viscosity coefficient grows with a power law behaviour, as function of the relative difference from the critical polymer concentration, characterized by a critical exponent k . The onset of the elastic response in the system, as function of the same control parameter, displays a power law increasing of the elastic modulus described by a critical exponent f [1]. This corresponds to the constitution inside the sol of a macroscopic polymeric structure [2], that characterizes the gel phase. As implicitly suggested in the work of Flory and Stockmayer [2], the percolation model is considered as the basic model for the chemical gelation transition and the macromolecular stress-bearing structure in these systems is a percolating network [3–5].

Moreover slow dynamics characterize the gelling solution: the relaxation functions in the experiments display a long time stretched exponential decay $\sim e^{-(\frac{t}{\tau_0})^\beta}$ as the gelation threshold is approached. The relaxation process becomes critically slow at the gel point, where the onset of a power law decay is typically observed [6].

Gelation phenomena are also observed in colloidal systems, that are suspensions of mesoscopic particles interacting via short range attraction: due to aggregation phenomena at low density (colloidal gelation) these systems display gel states with a power law behaviour of the viscosity coefficient and of the elastic modulus [7], as in chemical gelation. Yet the aggregation process gives rise to cluster-cluster aggregation producing a spanning cluster with a fractal dimensionality smaller than the random percolation case [8–11]. On the other hand with a weaker attraction at higher density a gelation charac-

terized by a glass-like kinetic arrest [12,13] may be observed. The relaxation patterns closely recall the ones observed in glassy systems and are well fitted by the mode-coupling theory [14] predictions for supercooled liquids approaching the glass transition [13]. On the theoretical side the application of the mode-coupling theory to systems with short range attractive interaction [15–17] (*attractive glasses*) has been recently considered and the connection with the colloidal glass transition has been proposed.

The question, that we want to investigate in this paper, is whether and to what extent colloidal gelation, colloidal glass transition and chemical gelation are related and if a unifying description is possible.

Let us first consider the case of the chemical gelation. By means of MonteCarlo numerical simulations on the cubic lattice we study a solution of tetrafunctional monomers. Each monomer occupies a lattice elementary cell and, to take into account the excluded volume interaction, two occupied cells cannot have common sites. At $t = 0$ we fix the fraction ϕ of present monomers respect to the maximum number allowed on the lattice, and randomly quench bonds between them. This actually corresponds to the typical chemical gelation process that can be obtained by irradiating the monomeric solution. The four possible bonds per monomers, randomly selected, are formed with probability p_b along lattice directions between monomers that are nearest neighbours and next nearest neighbours. Once formed, the bonds are permanent. The monomers diffuse on the lattice via random local movements and the bond length may vary but not be larger than l_0 according to bond-fluctuation dynamics [20]. The value of l_0 is determined by the self-avoiding walk condition and on the cubic lattice is $l_0 = \sqrt{10}$ in lattice spacing units. We let the monomers diffuse to reach the stationary state and then study the system for different values of the monomers concentration. We have considered $p_b = 1$, for which the system presents a percolation transition at $\phi_c = 0.718 \pm 0.005$. We have introduced this lattice model [18,19] to study the viscosity by means of the relaxation time, that diverges as function of ϕ at the percolation threshold with a power law behaviour [18]. The elastic response in the gel phase has been studied by means of the fluctuations in the free energy and grows with a power law behaviour as well as function of $(\phi - \phi_c)$ [19]. In this letter instead we present

a completely new study of the dynamics in gelation phenomena.

To investigate the nature of the dynamic transition at the chemical gelation here we study the equilibrium density fluctuation autocorrelation functions $f_{\vec{q}}(t)$ given by

$$f_{\vec{q}}(t) = \frac{\langle \rho_{\vec{q}}(t+t') \rho_{\vec{q}}(t') \rangle}{\langle |\rho_{\vec{q}}(t')| \rangle^2} \quad (1)$$

where $\rho_{\vec{q}}(t) = \sum_{i=1}^N e^{-i\vec{q} \cdot \vec{r}_i(t)}$, $\vec{r}_i(t)$ is the position of the i -th monomer at time t , N is the number of monomers and the average $\langle \dots \rangle$ is performed over the time t' . Due to the periodic boundary conditions the values of the wave vector \vec{q} on the cubic lattice are $\vec{q} = \frac{2\pi}{L}(n_x, n_y, n_z)$ with $n_x, n_y, n_z = 1 \dots L/2$ integer values.

We also study the mean square displacement of the particles $\langle \vec{r}^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle (\vec{r}_i(t+t') - \vec{r}_i(t'))^2 \rangle$.

In Fig.1 we present these time autocorrelation functions as function of the time calculated on a cubic lattice of size $L = 16$. The data have been averaged over ~ 10 up to 10^5 time intervals and over 20 different initial configurations of the sample. As the monomer concentration ϕ approaches the percolation threshold ϕ_c , $f_{\vec{q}}(t)$ displays a long time decay well fitted by a stretched exponential law $\sim e^{-(t/\tau)^\beta}$ with a $\beta \sim 0.30 \pm 0.05$. At the percolation threshold the onset of a power law decay is observed as it is shown by the double logarithmic plot of Fig.1 with an exponent c [6]. As the monomer concentration is increased above the percolation threshold in the gel phase, the long time power law decay of the relaxation functions can be fitted with a decreasing exponent c , varying from $c \sim 1$. at ϕ_c to $c \sim 0.2$ well above ϕ_c , where a nearly logarithmic decay appears. This behaviour well agrees with the one observed in gelling systems investigated in the experiments of refs. [6]. It is interesting to notice that this kind of decay with a stretched exponential and a power law reminds the relaxation behaviour found in spin-glasses [21].

The mean square displacement of the particles $\langle \vec{r}^2(t) \rangle$ presents a long-time diffusive behaviour and the diffusion coefficient decreases but remains finite also above ϕ_c . However the diffusion coefficient of clusters of size comparable with the connectedness length goes to zero at ϕ_c with the same exponent as the relaxation time [18]. In colloids the aggregation is due to a short range attraction and in general the monomers are not permanently bonded. To take into account this feature we introduce a novel ingredient in the previous model by considering a finite bond lifetime τ_b and study the effect on the dynamics. It is worth noticing that the features of this model with finite τ_b can be realized in a microscopic model: a solution of monomers interacting via an attraction of strength $-E$ and excluded volume repulsion. Due to monomers diffusion the aggregation process eventually takes place. The finite bond lifetime τ_b corresponds to an attractive interaction of strength

$-E$ that does not produce permanent bonding between monomers, and $\tau_b \sim e^{E/KT}$. A more detailed discussion will be available in a longer paper following up [22].

Due to the finite τ_b , in the simulations during the monomer diffusion the bonds between monomers are broken with a frequency $1/\tau_b$. Between monomers separated by a distance less than l_0 a bond is formed with a frequency f_b . For each value of τ_b we fix f_b so that the fraction of present bonds is always the same [22].

After the system has reached the equilibrium we have calculated $f_{\vec{q}}(t)$ as defined in eq.(1) and the relaxation time τ as $f_{\vec{q}}(\tau) \sim 0.1$.

Let us first analyze the behaviour of τ , plotted in Fig.2 as function of the monomer concentration ϕ for different τ_b . For comparison we have also shown the behaviour of τ in the case of permanent bonds, which displays a power law divergence at the percolation threshold ϕ_c . We notice that for finite bond lifetime τ_b the relaxation time increases following the permanent bonds case (chemical gelation), up to some value ϕ^* and then deviates from it. The longer the bond lifetime the higher ϕ^* is. In the high monomer concentration region, well above the percolation threshold, the relaxation time in the finite bond lifetime case again displays a steep increase and a power law divergence at some higher value. This truncated critical behaviour followed by a glassy-like transition has been actually detected in some colloidal systems in the viscosity behaviour [23,24].

These results can be explained by considering that only clusters whose diffusion relaxation time is smaller than τ_b will behave as in the case of permanent bonds. Larger clusters will not persist and their full size will not be relevant in the dynamics: the finite bond lifetime induces an effective cluster size distribution with a cut-off, which keeps the macroscopic viscosity finite [25]. As the concentration increases the final growth of the relaxation time is due to the crowding of the particles.

In Fig.3 $f_{\vec{q}}(t)$ is plotted as function of time for a fixed value of τ_b for increasing values of the monomer concentration (ϕ varies from below to well above $\phi_c = 0.718$). For small concentrations the autocorrelation function $f_{\vec{q}}(t)$ is well fitted by a stretched exponential decay, while for high monomer concentrations it exhibits a two-step decay, that closely resembles the one observed in supercooled liquids. We fit these curves using the mode-coupling β -correlator [14], corresponding to a short time power law $\sim f + \left(\frac{t}{\tau_s}\right)^{-a}$ and a long time von Schweidler law $\sim f - \left(\frac{t}{\tau_l}\right)^b$, giving the exponents $a \sim 0.33 \pm 0.01$ and $b \sim 0.65 \pm 0.01$ (the full lines in Fig.3). At long times the different curves obtained for different ϕ collapse into a unique master curve by opportunely rescaling the time via a factor $\tau(\phi)$. The master curve is well fitted by a stretched exponential decay with $\beta \sim 0.50 \pm 0.06$. The characteristic time $\tau(\phi)$ diverges at a

value $\phi_g \sim 0.96 \pm 0.05$ with the exponent $\gamma \sim 2.3 \pm 0.1$. This value well agrees with the mode-coupling prediction $\gamma = 1/2a + 1/2b$ [14].

In the inset the data are compared with the case of permanent bonds for two different values of ϕ . We observe that for short time (of the order of τ_b) the autocorrelation functions coincide with the permanent bond case.

A similar pattern, characterized by a plateau, is found in the mean square displacement $\langle \bar{r}^2(t) \rangle$ (Fig.4), with the diffusion coefficient going to zero as ϕ approaches ϕ_g . The inset also indicates that for short time the mean square displacement coincides with that calculated for the permanent bond case.

These results show that when bonds are permanent (chemical gelation) the divergence of the relaxation time is due to the formation of a macroscopic critical cluster and the autocorrelation function exhibits a one step decay related to the relaxation of such cluster. In the case of finite τ_b there is an effective cluster size distribution, as discussed above, and the autocorrelation function exhibits a two step relaxation which is well fitted by the mode coupling theory. This can be explained if we consider the system made of effective clusters playing the role of single molecules in an ordinary supercooled liquid or in a colloidal hard sphere system. As the monomer concentration increases, the relaxation time will diverge due to the jamming of the effective clusters. The first decay is due to the rattling and relaxation of the "effective" cluster in a cage made of surrounding clusters. The second relaxation is due, as usual, to the opening of the cage resulting in a structural relaxation. This picture supports the jamming of clusters that has been suggested on the basis of experimental observations on colloidal gelation in ref. [12]. For high temperature $\tau_b \rightarrow 0$, the clusters reduces to single monomers with a crossover to the usual phenomenology of the hard spheres glass transition.

When τ_b is large enough (strong attraction) the cluster effect will dominate and the slow dynamics will exhibit features more closely related to chemical gelation (Fig.1). The only difference is that in the limit $\tau_b \rightarrow \infty$ we expect that the spanning cluster will have the structure of the cluster-cluster irreversible aggregation model instead of random percolation.

In conclusion, these results suggest a unifying approach for chemical gelation, colloidal gelation and colloidal glass transition. In chemical gelation and colloidal gelation the cluster formation should produce the slow dynamics, that is expected to be of the same type of Fig. 1. In colloidal systems for weak attraction and high concentration the system crosses over from colloidal gelation to colloidal glass due to the jamming of effective clusters.

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- [1] M. Adam, D. Lairez, M. Karpasas and M. Gottlieb, *Macromolecules* **30** 5920 (1997)
 - [2] P.J.Flory *The Physics of Polymer Chemistry* Cornell University Press (Ithaca) 1954
 - [3] P.G. de Gennes *Scaling concepts in polymer physics* Cornell University Press (Ithaca) 1980
 - [4] D. Stauffer *Physica A* **106** 177 (1981)
 - [5] D. Stauffer, A. Coniglio and M. Adam, *Adv.in Polymer Sci.* **44** 103 (1982)
 - [6] J.E. Martin, J.P. Wilcoxon and J. Odinek, *Phys. Rev. A* **43** 858 (1991); F.Ikkai and M.Shibayama, *Phys. Rev. Lett.* **82** 4946 (1999); S.Z.Ren and C.M.Sorensen, *Phys.Rev.Lett.* **70** 1727 (1993); P.Lang. and W.Burchard *Macromolecules* **24** 815 (1991)
 - [7] V. Trappe, V. Prasad, L. Cipelletti, P.N. Segre and D.A. Weitz, *Nature* **411** 772 (2001); V. Trappe and D.A. Weitz *Phys.Rev.Lett.* **85** 449 (2000)
 - [8] P. Meakin *Phys. Rev. Lett* **51** 1119 (1983)
 - [9] R. Jullien and A. Hawsmys *Phys. Rev. Lett.* **74** 4003 (1995)
 - [10] J.C. Gimel, T. Nicolai, D. Durand *J. Sol-gel Sci. Technol.* **15** 129 (1999)
 - [11] A.D. Dinsmore and D.A. Weitz *J. Phys. : Condens. Matter* **14** 7581 (2002)
 - [12] P. N. Segré, V. Prasad, A. B. Schofield, and D. A. Weitz *Phys. Rev. Lett.* **86** 6042 (2001)
 - [13] H. Gang, A. H. Krall, H. Z. Cummins, and D. A. Weitz, *Phys. Rev. E* **59** 715 (1999); F. Mallamace, P. Gambadauro, N. Micali, P. Tartaglia, C. Liao and S.H. Chen, *Phys.Rev.Lett.* **84** (2000) 5431
 - [14] W.Göetze in *Liquid, Freezing and Glass Transition*, eds. J.P. Hansen, D. Levesque and P. Zinn-Justin, Elsevier (1991)
 - [15] L. Fabbian, W. Götze, F. Sciortino, P. Tartaglia and F. Thiery, *Phys. Rev. E* **59**, R1347 (1999); **60**, 2430 (1999); J. Bergenholtz, M. Fuchs, and Th. Voigtmann, *J. Phys. : Condens. Matter* **12**, 4341 (2000)
 - [16] K. Dawson, G. Foffi, M. Fuchs, W. Götze, F. Sciortino, M. Sperl, P. Tartaglia, Th. Voigtmann and E. Zaccarelli, *Phys. Rev. E* **63** 011401 (2001); E. Zaccarelli, G. Foffi, K. A. Dawson, F. Sciortino and P. Tartaglia, *Phys. Rev. E* **63**, 031501 (2001)
 - [17] A.M. Puertas, M. Fuchs and M.E. Cates *cond-mat/0211087*; M.E. Cates to appear in *Annales Henri Poincare*; A.M. Puertas, M. Fuchs and M.E. Cates *Phys.Rev.Lett.* **88** (2002) 098301
 - [18] E.Del Gado, L. de Arcangelis and A. Coniglio *Eur. Phys. J. B* **2** 352 (2000)
 - [19] E. Del Gado, L. de Arcangelis and A. Coniglio *Phys.Rev.E* **65** 041803 (2002)
 - [20] I. Carmesin and K. Kremer *Macromolecules* **21** 2819 (1988)
 - [21] A. T. Ogielski *Phys. Rev. B* **32** 7384 (1985)
 - [22] E. Del Gado, L. de Arcangelis and A. Coniglio in preparation
 - [23] F. Mallamace, S.H. Chen, Y. Liu, L. Lobry and N. Micali

Physica A **266** (1999); F. Mallamace, R. Beneduci, P. Gambadauro, D. Lombardo and S.H. Chen, Physica A **302** 202 (2001)

[24] F. Laffèche, D. Durand and T. Nicolai *preprint* (2002)

[25] A. Coniglio J. Phys. : Condensed Matter **13** 9039 (2001)

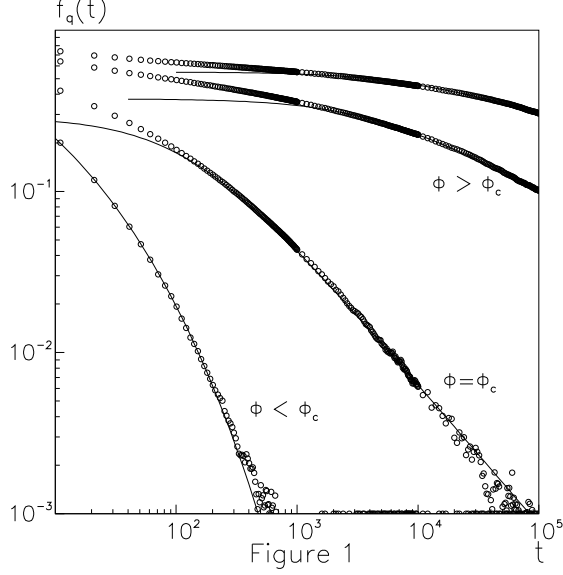


FIG. 1. Double logarithmic plot of the autocorrelation functions $f_{\bar{q}}(t)$ as function of the time for $q \sim 1.36$ and $\phi = 0.6, 0.718, 0.8, 0.85$. For $\phi < \phi_c$ the long time decay is well fitted by a function (full line) $\sim e^{-(t/\tau)^\beta}$ with $\beta \sim 0.3$. At the percolation threshold and in the gel phase in the long time decay the data are well fitted by a function $\sim (1 + \frac{t}{\tau})^{-c}$.

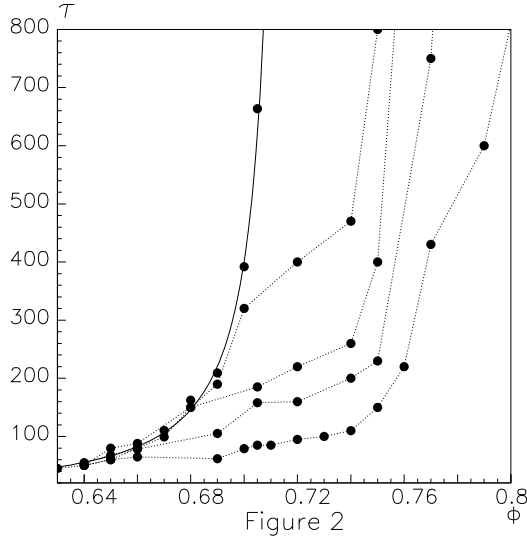


Figure 2

FIG. 2. The average relaxation time as function of the density; from left to right: the data for the permanent bonds case diverge at the percolation threshold with a power law (the full line); the other data refer to finite $\tau_b = 3000, 1000, 400, 100 MCstep/particle$ decreasing from left to right (the dotted lines are a guide to the eye)

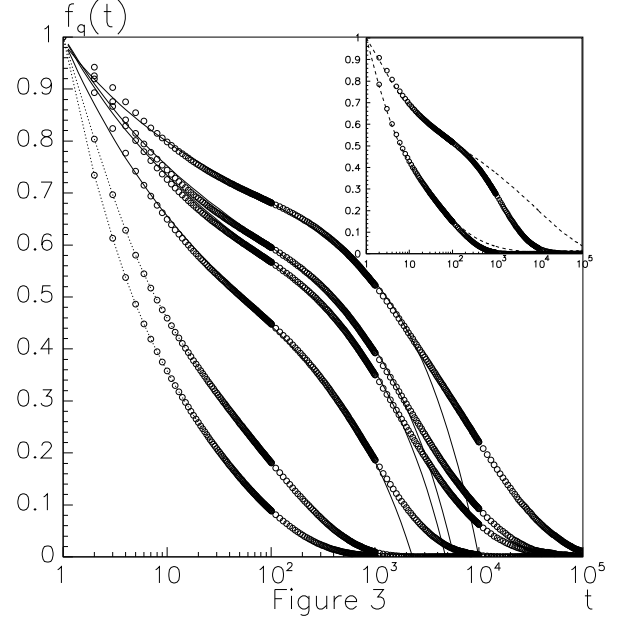


FIG. 3. The $f_{\bar{q}}(t)$ as function of the time for $q \sim 1.36$ calculated on a cubic lattice of size $L = 16$ for $\tau_b = 1000 MCstep/particle$. (from left to right $\phi = 0.6, 0.718, 0.8, 0.85, 0.87, 0.9$). The full lines correspond to the fit with the mode-coupling *beta*-correlator. In the inset, the data for $\phi = 0.718$ and $\phi = 0.8$ (from left to right) are plotted together with the ones obtained at the same densities in the case of permanent bonds (dashed line).

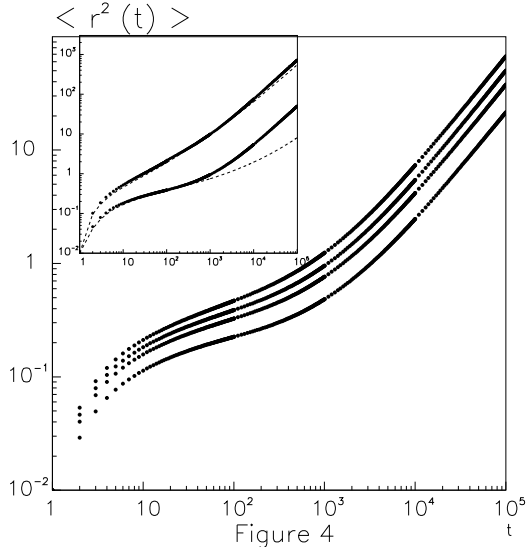


FIG. 4. The mean-square displacement $\langle \vec{r}^2(t) \rangle$ of the particles as function of the time in a double logarithmic plot for $\tau_b = 1000 MCstep/particle$: from top to bottom $\phi = 0.8, 0.82, 0.85, 0.9$, approaching ϕ_g . In the inset $\langle \vec{r}^2(t) \rangle$ for the same ϕ for $\tau_b = 1000 MCS/particle$ and in the case of permanent bonds (dashed line) (from top to bottom, $\phi = 0.718, 0.8$)